

# Degradation of chlorophenoxyacid herbicides in aqueous media, using a novel electrochemical method<sup>†</sup>

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**Abstract:** The degradation of five chlorophenoxyacid herbicides has been studied using an electrochemical method based on the Fenton reaction (simultaneous reduction of dioxygen and ferric ions). The method consists of electrosynthesizing OH<sup>•</sup> radicals, which react rapidly with chlorophenoxyacids in aqueous media. HPLC and GC-MS analysis show the formation of polyhydroxyphenols and quinones in a first step, and the complete destruction of the aromatic nucleus upon exhaustive electrolysis. This offers a possible way for the depollution of natural waters containing chlorophenoxyacid pesticide residues.

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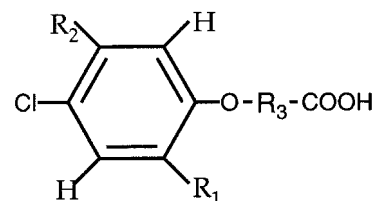
**Keywords:** chlorophenoxy acid herbicides; electro Fenton reaction; water depollution

## 1 INTRODUCTION

Chlorophenoxyacid herbicides are widely used for agricultural and non-agricultural purposes in France and many other European countries; they are employed on a large scale for pre- and post-emergence weed control of corn, wheat, sorghum and barley, and on railways, roadside and verges. Not surprisingly, they have been detected at relatively high levels in ground and surface waters throughout Europe.<sup>1</sup>

Because of this widespread use, chlorophenoxy acid herbicides constitute ubiquitous, organic pollutants of the environment, being especially present in natural waters, where, they are of concern, because of their potential toxicity towards humans and animals.<sup>2</sup> Therefore, it is very important to develop a simple, rapid and cheap method allowing degradation of these herbicides into less toxic compounds.

In the present study, we propose a new method based on the electrosynthesis of hydroxyl radicals (OH<sup>•</sup>) for the degradation of selected chlorophenoxy acid pesticides (Fig 1). OH<sup>•</sup> radicals are extremely reactive species which play an important role in a number of chemical and biological processes.<sup>3,4</sup> In aqueous solutions, OH<sup>•</sup> radicals can be easily electro-synthesized and are very strong one-electron oxidizing agents ( $E^{\circ}_{(\text{OH}^{\bullet}, \text{H}^+/\text{H}_2\text{O})} = 2.72 \text{ V/NHE}^4$  at pH=0 and  $E^{\circ}_{(\text{OH}^{\bullet}/\text{OH}^-)} = 1.89 \text{ V/NHE}$ ),<sup>4–6</sup> although they rarely



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
CPMP	H	H	-C(CH <sub>3</sub> ) <sub>2</sub> -
CMPP	CH <sub>3</sub>	H	-CH(CH <sub>3</sub> )-
2,4-D	Cl	H	-CH <sub>2</sub> -
2,4-DP	Cl	H	-CH(CH <sub>3</sub> )-
2,4,5-T	Cl	Cl	-CH <sub>2</sub> -

**Figure 1.** Chemical structures of chlorophenoxyacid herbicides under study.

behave as electron-transfer reagents. They are very reactive species in hydrogen atom abstractions and in electrophilic additions.<sup>6,7</sup> The complex mechanism of addition of OH<sup>•</sup> to a variety of aromatic derivatives is well documented;<sup>7–12</sup> the first and very fast ( $k \sim 10^9$ – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) step of OH<sup>•</sup> addition to an aromatic ring leads to the formation of a hexadienyl radical. In the presence of an oxidizing agent such as O<sub>2</sub>, Fe<sup>3+</sup> or Cu<sup>2+</sup>, hydroxylated aromatic derivatives are obtained and more extensive reactions, leading to destruction of

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the aromatic moiety and formation of oxidized, simple aliphatic molecules may take place.<sup>13-17</sup> In the present work, we investigate the formation of polyhydroxylated products, resulting from  $\text{OH}^\bullet$  reaction with selected chlorophenoxy acid pesticides in aqueous media and show that the reaction proceeds to the complete destruction of the aromatic nucleus upon exhaustive electrolysis. The method could be applied to the depollution of water samples containing chlorophenoxyacid pesticide residues.

## 2 EXPERIMENTAL

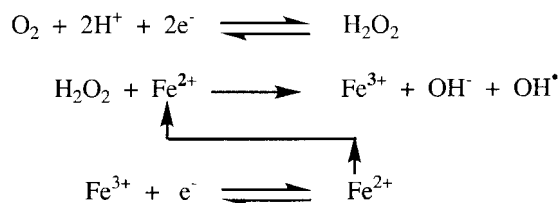
### 2.1 Chemicals

2-(4-Chloro-2-methylphenoxy)propionic acid (CMPP) was obtained from Lancaster, while 2,4-dichlorophenoxyacetic acid (2,4-D), 2-(4-chlorophenoxy)-2-methylpropionic acid (CPMP), 2-(2,4-dichlorophenoxy)propionic acid (2,4-DP) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and chlorophenols used as standards, as well as solvents (methanol, acetic acid) were purchased in the highest purity available from Aldrich. Distilled water was used.

### 2.2 Electrochemical procedure

Electrolyses were carried out in a 100-ml three-electrode electrochemical cell as previously described.<sup>11</sup> The working electrode was a 15-cm<sup>2</sup> mercury pool. The platinum counter-electrode was placed in the anode compartment separated from the cathode compartment by a no. 4 glass frit. The reference electrode was a saturated calomel electrode (SCE). All pesticides were dissolved in hydrochloric acid (0.01 M). Initial concentrations of the electrolyzed solutions were 0.5 mM for 2,4,5-T and 1.0 mM for the remaining pesticides. Prior to the electrolysis, dioxygen was bubbled for 10 min and then 78 mg of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$  was introduced in 100 ml aqueous solution ( $[\text{Fe}^{2+}] = 2 \text{ mM}$ ).

The cathode potential was maintained at  $-0.5 \text{ V/SCE}$  with a laboratory-made potentiostat, a potential where both  $\text{O}_2$  and  $\text{Fe}^{3+}$  are reduced respectively to  $\text{O}_2^{\bullet -}$  and  $\text{Fe}^{2+}$  while continuously bubbling oxygen ( $c = 1.3 \times 10^{-3} \text{ M}$ ). In these conditions, the current remained constant (about 65–70 mA) during the electrolysis, allowing the production of a constant



**Figure 2.** Production scheme of  $\text{OH}^\bullet$  radicals, based on the electrochemical Fenton reaction.

amount of  $\text{OH}^\bullet$  radicals. The charge passing through the solution was measured with a Tacussel IG5-N coulometer. An EG&G electrochemical system model 273 A was also used to perform some experiments.

### 2.3 Chromatographic analysis

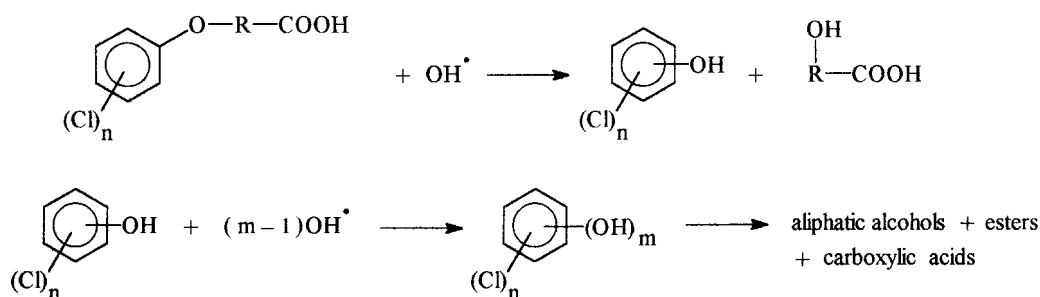
During electrolysis, samples were withdrawn at regular charge intervals, (0, 50, 100, 150, 200... 500 C) and analysed in a HPLC apparatus (Gilson) equipped with a UV detector set at 282 nm and driven with a microcomputer. A Hypersil-C 18 column (25 cm  $\times$  4.6 mm) was used. The elution solvent was methanol+water+acetic acid (53+45+2 by volume) at  $0.7 \text{ ml min}^{-1}$ .

In order to identify the chlorophenoxyacid pesticide degradation products, a GC-MS analysis was performed. After electrolysis, the aqueous solutions were filtered and extracted three times with dichloromethane. The aqueous and organic phases were examined by means of HPLC, and, the dichloromethane solution was then concentrated by evaporation of the solvent to a volume of about 2 ml, and analysed in a GC-MS instrument (QMD-1000 Carlo Erba), equipped with a 30-m Quadrex fused silica capillary column packed with methyl 5% phenylsilicone. A gradient temperature program at  $5^\circ \text{C min}^{-1}$  was used between 50 and  $250^\circ \text{C}$ .

## 3 RESULTS AND DISCUSSION

### 3.1 Principle

The production of the  $\text{OH}^\bullet$  radicals takes place in two steps: (1) electrochemical reduction of dioxygen into superoxide ion ( $\text{O}_2^{\bullet -}$ ) and formation of  $\text{H}_2\text{O}_2$  in an acidic medium; (2) reaction of  $\text{H}_2\text{O}_2$  with  $\text{Fe}^{2+}$  ions yielding  $\text{OH}^\bullet$  radicals (Fenton reaction)<sup>18,19</sup> (Fig 2). In these conditions,  $\text{Fe}^{3+}$  ions are electrochemically



**Figure 3.** Mechanism of the addition reaction of the  $\text{OH}^\bullet$  radical on the chlorophenoxyacid aromatic moiety and further reactions.  $n$ =number of chlorine substituents ( $1 \leq n \leq 3$ );  $m$ =number of hydroxy groups ( $m < 4$ ).

**Table 1.** Identification and distribution of chlorophenoxyacid pesticide degradation products during electrolysis at various coulombic charges (Q).

Compound	Q (C)	Remaining pesticide (%)	Monohydroxy derivative <sup>a</sup>	Dihydroxy derivative <sup>b</sup>	Trihydroxy derivative <sup>c</sup>	Others <sup>d</sup>
CPMP	200	27	4-Cl PhOH <sup>e</sup>	–	–	
	400	10	4-Cl PhOH <sup>e</sup>	1,2-diOH-4 Cl Bz <sup>f</sup>	–	1,4-BzQ <sup>f</sup> , aliphatic compounds
MCPMP	50	56	4-Cl 2-Me PhOH <sup>e</sup>	–	–	
	100	36	4-Cl 2-Me PhOH <sup>e</sup>	5-Cl 1,2-diOH 3-Me Bz <sup>e</sup>	–	
	200	20	4-Cl 2-Me PhOH <sup>e</sup>	5-Cl 1,2-diOH 3-Me Bz <sup>e</sup>	6-Cl 1,2,3-tri OH 4-MeBz	–
2,4-D	150	5	2,4 diCl PhOH <sup>e</sup>	–	–	
	200	0	2,4 diCl PhOH <sup>e</sup>	1,2-diOH4,6-diClBz <sup>f</sup>	1,2,3-triOH 4,6-diClBz <sup>f</sup>	2-Cl 1,4-BzQ <sup>f</sup>
	350	0	–	1,2-diOH4,6-diClBz <sup>f</sup>	1,2,3-triOH 4,6-diClBz <sup>f</sup>	Aliphatic compounds
2,4-DP	50	30	2,4-diCl PhOH <sup>e</sup>	–	–	
	220	0	2,4-diCl PhOH <sup>e</sup>	1,2-diOH 4,6-diClBz <sup>f</sup>	–	Aliphatic compounds
	250	0	–	1,2-diOH 4,6-diClBz <sup>f</sup>	–	Aliphatic compounds
	500	0	–	1,2-diOH 4,6-diClBz <sup>f</sup>	1,2,3-triOH 4,6-diClBz <sup>f</sup>	Aliphatic compounds
2,4,5-T	50	30	2,4,5-triCl PhOH <sup>e</sup>	3,5,6-triCl 1,2-diOHBz	–	Aliphatic compounds
	150	5	2,4,5-triCl PhOH <sup>e</sup>	3,5,6-triCl 1,2-diOHBz	–	Aliphatic compounds
	600	0	–	–	–	Aliphatic compounds

<sup>a</sup> 4-Cl PhOH = 4-chlorophenol; 4-Cl 2-MePhOH = 4-chloro 2-methylphenol; 2,4-diClPhOH = 2,4-dichlorophenol; 2,4,5-triClPhOH = 2,4,5-trichlorophenol.

<sup>b</sup> 1,2-diOH 4-Cl Bz = 1,2-dihydroxy 4-chlorobenzene; 5-Cl 1,2-diOH 3-MeBz = 5-chloro 1,2-dihydroxy 3-methylbenzene; 1,2-diOH 4,6-diClBz = 1,2-dihydroxy 4,6-dichlorobenzene; 3,5,6-triCl 1,2-diOHBz = 3,5,6-trichloro 1,2-dihydroxy benzene.

<sup>c</sup> 6-Cl 1,2,3-triOH 4-MeBz = 6-chloro 1,2,3-trihydroxy 4-methylbenzene; 1,2,3-triOH 4,6-diClBz = 1,2,3-trihydroxy 4,6-dichlorobenzene.

<sup>d</sup> 1,4-BzQ = 1,4-benzoquinone; 2-Cl 1,4-BzQ = 2-chloro-1,4-benzoquinone.

<sup>e</sup> Derivative identified by HPLC analysis, using a standard.

<sup>f</sup> Derivative identified by GC-MS analysis.

reduced to Fe<sup>2+</sup> ions (Fe<sup>3+</sup>/Fe<sup>2+</sup> electrocatalytic system).

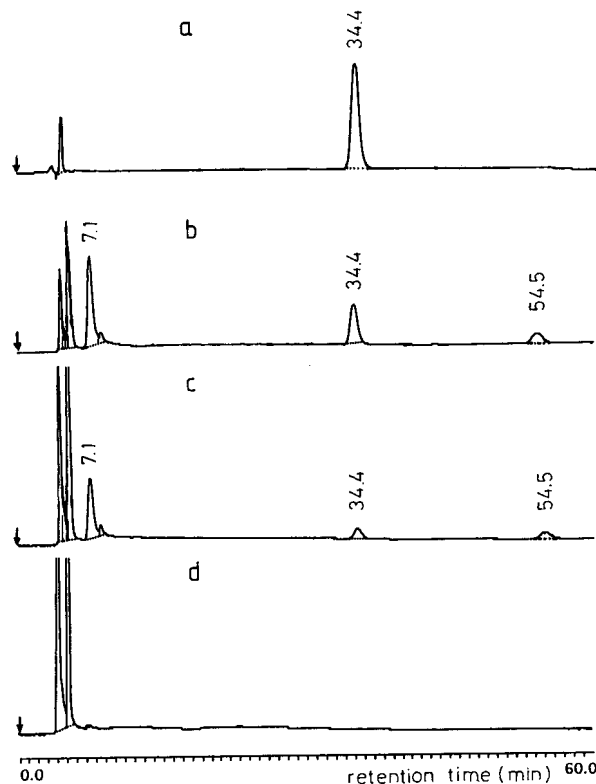
It is expected that the chlorophenoxyacid pesticides will react with OH<sup>-</sup> according to the different reactions summarized in Fig 3.

### 3.2 HPLC and GC-MS studies

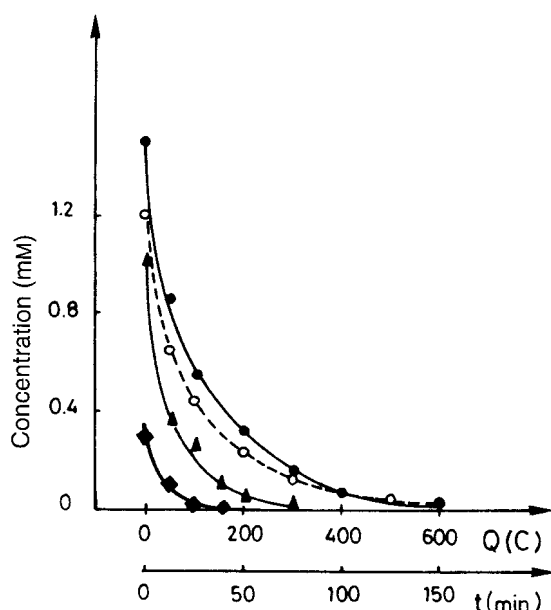
HPLC analysis permits the monitoring of the disappearance of the chlorophenoxyacid pesticides during electrolysis as well as the formation and/or destruction of reaction products. Table 1 summarizes the identification of degradation products formed at various coulombic charges for the four chlorophenoxyacid herbicides under study. In all cases and for low coulombic charges, (starting at Q ≈ 0 C, according to the compound) the chromatograms show the formation of significant concentrations of mono-, di- or trichlorophenol (Fig 2).

For higher coulombic charges (Q ~ 100–200 C, depending on the compound), new peaks, corresponding to di- and trihydroxychlorobenzene derivatives, are observed in the chromatograms. The identification of these products is confirmed by HPLC analysis of authentic samples (standards) as well as by a GC-MS study. Also, the formation of small amounts of quinones or chloroquinones is revealed by GC-MS analysis (Table 1).

Upon applying even higher coulombic charges (Q ~ 200–600 C), hydroxychlorobenzene derivatives disappear progressively; the appearance of aliphatic



**Figure 4.** HPLC chromatograms recorded at different coulombic charges for the electrolysis of 2,4,5-T ( $3.1 \times 10^{-4}$  M) by electrochemically generated OH<sup>-</sup> (a) 0 C; (b) 50 C; (c) 150 C; (d) 200 C. The peaks at 7.1 min, 34.4 min and 54.5 min correspond respectively to the dihydroxy derivatives, 2,4,5-T and the monohydroxy derivative.



**Figure 5.** Kinetics of degradation of (—●—) MCPMP; (---○---) CPMP; (—▲—) 2,4-DP and (---◆---) 2,4,5-T. The time-scale was established using an electrolysis current of 65 mA. Initial concentrations were respectively: 1.50 mM for MCPMP, 1.20 mM for CPMP, 1.00 mM for 2,4-DP and 0.30 mM for 2,4,5-T.

alcohols, ketones, carboxylic acids and alkenes is indicated by GC-MS analysis.

A striking example of this behaviour is provided by the case of the electrolysis of 2,4,5-T (Fig 4). As can be seen, mono- and di-hydroxytrichlorobenzene derivatives are formed in significant amounts for a low coulombic charge ( $Q=50$  C) (Fig 4, curve b). These derivatives are hydroxylated rapidly and the aromatic ring is destroyed, leading to the formation of aliphatic products for  $Q=150$  C (Fig 4, curve c). Practically, all aromatic derivatives have disappeared for  $Q=200$  C (Fig 4, curve d). At the end of the electrolysis, the energy consumption amounts to  $8.5 \times 10^{-5}$  kWh for 100 ml of a 0.5 mM solution of 2,4,5-T.

### 3.3 Kinetic and mechanistic studies

Figure 5 shows the evolution of chlorophenoxyacid herbicide concentration with coulombic charge and electrolysis time. The kinetic curves are characterized by a rapid and regular decrease of the herbicide concentration during electrolysis.

It can be seen that increasing the number of chlorine substituents on the aromatic ring produces an enhancement of the hydroxylation reaction rate; this result can be rationalized by the additive, mesomer electron-donor (+M) effects of chlorine groups, which would stabilize the corresponding cyclohexadienyl radical and/or radical-cations involved in the hydroxylation mechanism.<sup>11</sup> Also, the electricity amount required for electrolysis is diminished in the presence of an increasing number of chlorine atoms, since the number of reactive sites is decreased, leading to a reduction of the number of intermediate products.

The product distribution results (obtained at the beginning of the electrolysis) suggest that, in a first step, a dissociation of the Ph-ORCO<sub>2</sub>H bond is

provoked by an attack of the hydroxyl radical on the aromatic moiety of the pesticide under study, yielding mono-, di- or trichlorophenols (CMPs). In a second step, corresponding to higher coulombic charges, the electrophilic OH<sup>•</sup> radical would react with the free, activated *ortho* position of the mono- di- or trichlorophenol hydroxy group leading to formation of mono-, di- or trichlorodiphenols (CDPs) according to the herbicide structure (Table 1). The explanation is in agreement with the fact that the concentration of the CMPs increases rapidly at the beginning of the electrolysis, to reach a steady concentration at about 200–400 C (at which values the CMP hydroxylation rate becomes larger than the formation rate), and then diminishes.

In subsequent reactions, occurring at even higher coulombic charges, CDPs in their turn are hydroxylated and/or oxidized into quinones. Furthermore, polyhydroxylated chlorobenzene derivatives and quinones would be attacked by OH<sup>•</sup> radicals, resulting in opening of the benzene ring and successive loss of carbon atoms, leading to the appearance of aliphatic alcohols, ketones and carboxylic acids. Our results confirm the hypothesis proposed for the reaction mechanism (Fig 3). They are also in agreement with a recent study of Merga *et al.*,<sup>17</sup> concerning the hydroxylation of chlorobenzene in aqueous solution by radiolytically generated OH<sup>•</sup> radicals.

For environmental purposes, our method could be applied to the rapid destruction of chlorophenoxy acid herbicides contained in natural waters at the millimolar level.

### CONCLUSION

We have shown for the first time that chlorophenoxy acids can be hydroxylated step by step in the presence of electrogenerated hydroxyl radicals. The main interest of this method is that, following rapid polyhydroxylation, the aromatic ring of chlorophenoxy acid herbicides can be destroyed, leading to the formation of less toxic aliphatic products. Therefore, this electrochemical approach can be considered as very clean and well suited for decontaminating natural waters containing pollutants. Indeed, the electrocatalysed production of Fenton reagent ( $H_2O_2 + Fe^{2+}$ ) requires only the use of a simple electrochemical system instead of chemical reagents, resulting in a potential low-cost and non-polluting method of destruction of pesticide residues.

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